

## Lateral hopping of CO on Cu(111) induced by femtosecond laser pulses

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We present a theoretical study of the lateral hopping of a single CO molecule on Cu(111) induced by femtosecond laser pulses by Mehlhorn *et al.* [*Phys. Rev. Lett.* **104**, 076101 (2010)]. Our model assumes an intermode coupling between the CO frustrated translation (FT) and frustrated rotation (FR) modes with a weak and strong electronic friction coupling to hot electrons, respectively, and heat transfer between the FT mode and the substrate phonons. In this model the effective electronic friction coupling of the FT mode depends on the absorbed laser fluence  $F$  through the temperature of the FR mode. The calculated hopping yield as a function of  $F$  nicely reproduces the nonlinear increase observed above  $F=4.0$  J/m<sup>2</sup>. It is found that the electronic heating via friction coupling nor the phonon coupling alone cannot explain the experimental result. Both heatings are cooperatively responsible for CO hopping on Cu(111). The electronic heat transfer dominates over the phononic one at high  $F$ , where the effective electronic friction coupling becomes larger than the phononic coupling.

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Real-space and/or real-time monitoring of adsorbate motions and chemical reactions on surfaces are the ultimate techniques to study adsorbate reaction dynamics. The first real-space observation of molecular motion induced by femtosecond laser pulses has been made in combination with a scanning tunneling microscope (STM) by Bartels *et al.*<sup>1</sup> for CO on Cu(110). They combined direct imaging of a single CO molecule by STM with femtosecond laser excitation. They found that electronic excitation of the substrate induced by absorption of short laser pulses gives rise to hopping of CO parallel and perpendicular to the close-packed rows, in addition to desorption. STM, which permits a direct imaging of a single molecule before and after laser irradiation, cannot be used to monitor laser-induced adsorbate motions on ultrafast time scale while nonlinear time-resolved optical spectroscopy with unique high surface sensitivity enables adsorbate motions to be monitored on the time scale typically involved in adsorbate dynamics.<sup>2</sup>

Recently Mehlhorn *et al.*<sup>3</sup> have reported on femtosecond-laser-induced hopping of a single CO molecule on Cu(111) using a scanning tunneling microscope. As a function of the absorbed laser fluence  $F$ , they observed that the hopping yield  $Y(F)$  exhibits a linear increase at low  $F$ , followed by a strongly nonlinear increase at high  $F$ . They proposed that the linear increase arises from single electronic transitions dynamics induced by electronic transition (DIET),<sup>4</sup> while the strong increase can be described using a friction model, where hot electrons transfer energy to the frustrated translation (FT) mode. They assumed the electronic friction  $\eta_{el}$  to depend on the electron temperature  $T_{el}(t)$ , in accordance with earlier suggestions.<sup>5</sup> However, it was proved that frictional coupling is temperature independent if it originates from electron-hole pair excitation.<sup>6,7</sup> The electronic friction is defined as  $\eta_{el}=w_{1\rightarrow 0}-w_{0\rightarrow 1}$ , where the decay rate  $w_{1\rightarrow 0}$  and the thermal excitation rate  $w_{0\rightarrow 1}$  between the vibrational excited state and the ground state is given by  $\eta_{el}(n_B+1)$  and  $\eta_{el}n_B$ , respectively, and where  $n_B=[\exp(\hbar\Omega/k_B T)-1]^{-1}$  is the

Bose-Einstein distribution function of a vibrational mode with the energy  $\hbar\Omega$ . It is clear that  $\eta_{el}$  is temperature *independent*, even when  $w_{1\rightarrow 0}$  and  $w_{0\rightarrow 1}$  depend on the temperature. Empirical  $T_{el}$ -dependent friction model with  $\eta_{el}=\eta_{el}^0 T_{el}^n(t)$  have also been used to explain the two-pulse correlation and the  $F$  dependence of atomic oxygen and CO hopping on stepped Pt(111) (Refs. 8 and 9) and desorption of oxygen molecules from Pd(111).<sup>10</sup> In spite of these apparent successes in describing the experimental results, there is no theoretical arguments supporting the use of a  $T_{el}$ -dependent friction.

Here we show how one can understand the experimental results of Ref. 3 without using a temperature-dependent friction. We propose an indirect heating of the FT mode via the intermode coupling with the FR mode, in addition to a direct heating of the FT mode by laser excitation.<sup>11</sup> Dobbs and Doren<sup>12</sup> have shown for CO on Ni(111) that the bending and the lateral translational motions are strongly coupled near the transition state for hopping. From the synchrotron infrared studies of the CO/Cu(111) system<sup>13</sup> one can determine the electronic friction  $\eta_{FT}=1/(60$  ps). Using this small  $\eta_{FT}$  direct heating of the FT mode cannot reproduce the strongly nonlinear increase in the hopping yield at high  $F$ . For this reason Mehlhorn *et al.*<sup>3</sup> had to use an electronic friction which depends on the electron temperature in order to reproduce their experimental results. The friction coupling to the frustrated rotation (FR) mode [ $\eta_{FR}=1$ /ps (Ref. 13)] is 60 times stronger than the coupling to the FT mode and encourages us to employ our mode-coupling model for an indirect heating of the FT mode.

The coupled equations for heat transfer via the FT-FR mode coupling are given by,<sup>11</sup>

$$dU_{FT}/dt = [\eta_{FT} + (\eta_{FT,FR}/\hbar\Omega_{FR})U_{FR}](U_{el} - U_{FT}) + \eta_{ph,FT}(U_{ph} - U_{FT}), \quad (1)$$

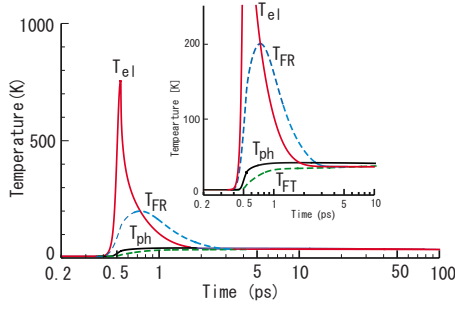


FIG. 1. (Color online) Transient temperature of  $T_{el}(t)$  (red curve),  $T_{ph}(t)$  (black curve),  $T_{FR}(t)$  (dashed blue curve), and  $T_{FT}(t)$  (dashed green curve) calculated at  $F=4.3$  J/m<sup>2</sup>. See the text for the parameters used herein.

$$dU_{FR}/dt = [\eta_{FR} + (\eta_{FR,FT}/\hbar\Omega_{FT})U_{FT}](U_{el} - U_{FR}) + \eta_{ph,FR}(U_{ph} - U_{FR}), \quad (2)$$

where  $U_x = \hbar\Omega/[exp(\hbar\Omega/k_B T_x) - 1]$  denotes the energy of a harmonic oscillator corresponding to the FT and FR mode ( $\hbar\Omega_{FT}=4$  meV,  $\hbar\Omega_{FR}=35$  meV) at the temperature  $T_x$  (where  $x=FT, FR, el$ , and  $ph$  indicate the FT mode, FR mode, and hot electrons and phonons, respectively). Here  $\eta_{ph,i}$  ( $i=FT, FR$ ) is the phonon coupling with the FT and FR mode. We include phononic coupling, not only for completeness but also because  $\eta_{FT} \ll \eta_{ph,FT}=0.07/\text{ps}$  (Ref. 14) and assume  $\eta_{ph,FR}=0$  because the time scale of heating the FR mode is mainly determined by the large electronic friction of  $\eta_{FR}=1/\text{ps}$ . Note that in our model the effective electronic heat transfer coefficient between the substrate electrons and the FT mode is given by

$$\eta_{eff,FT}(t) = \eta_{FT} + (\eta_{FT,FR}/\hbar\Omega_{FR})U_{FR}(t), \quad (3)$$

which depends on  $F$  through  $T_{FR}(t)$ .

Equations (1) and (2) are combined with the so-called two-temperature model<sup>15</sup> to calculate  $T_{el}(t)$  and  $T_{ph}(t)$  using the material parameters of Cu (electron-phonon coupling, heat capacity, and thermal conductivity of electrons and phonons, and Debye temperature) in Ref. 16. The initial substrate temperature is 7 K and a  $\text{sech}^2$ -shaped pulse with a duration of 40 fs at 400 nm is used for a laser source. Figure 1 shows the time evolution of  $T_{el}(t)$  (red curve),  $T_{ph}(t)$  (black curve),  $T_{FT}(t)$  (dashed blue curve), and  $T_{FR}(t)$  (dashed green curve) following the laser-pulse irradiation at 0.5 ps with  $F=4.3$  J/m<sup>2</sup>. The parameters used here are all obtained in independent measurements<sup>13</sup> ( $\eta_{FT}=0.016/\text{ps}$ ,  $\eta_{FR}=1/\text{ps}$ ) except for the mode-coupling parameter  $\eta_{FT,FR}$ , for which we use 1.2/ps in order to obtain the best agreement with the experimental result of  $Y(F)$  shown below. The transient profile of  $\eta_{eff,FT}(t)$  shown in Fig. 2 follows that of  $T_{FR}(t)$  and increases with  $F$ . As shown in Fig. 1 the FR mode reaches the maximum temperature of 200 K less than at 1 ps. In contrast since  $\eta_{eff,FT}(t) \ll \eta_{FR}$ ,  $T_{FT}(t)$  exhibits a quite gradual increase up to only about 40 K for  $F=4.3$  J/m<sup>2</sup> and an extremely slow cooling extending over nanoseconds before the subsystem reaches thermal equilibrium ( $T_{el}=T_{ph}$ ). We note

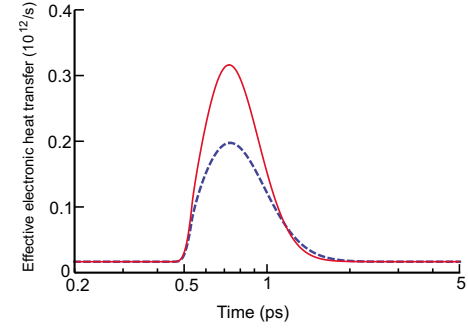


FIG. 2. (Color online) Transient effective heat transfer coefficient  $\eta_{eff,FT}(t)$  at  $F=4.3$  (dashed blue curve) and 5.3 (red curve) J/m<sup>2</sup>.

that thermal hopping of a single CO molecule on a Cu(110) was monitored in the temperature range between 42 and 53 K with STM.<sup>17</sup>

The dependence of a hopping yield  $Y(F)$  on  $F$  is given by a sum of the linear and nonlinear part,

$$Y(F) = \alpha F + \int R(t, F) dt, \quad (4)$$

$$R(t, F) = R_0 \exp[-E_b/k_B T_{FT}(t, F)], \quad (5)$$

where  $\alpha=1.0 \times 10^{-9}$  per pulse and per joule per square meter is used in order to fit the linear part of the experimental result and the same barrier height  $E_b=87$  meV as used in the analysis in Ref. 3. This is close to  $E_b=97 \pm 4$  meV deduced from thermal diffusion data for CO on Cu(110).<sup>17</sup> We calculate  $Y(F)$  using  $R_0=1.43 \times 10^{13}/\text{s}$ . The prefactor  $R_0$  for a thermally activated process is the attempt rate, which usually is comparable to the frequency of the vibrational mode along the reaction coordinate. Thus we expect  $R_0=10^{12}-10^{13}/\text{s}$  for isolated CO on Cu. The  $R_0$  we use is close to what one expects from Kramers theory of activated processes, which in the present case gives  $R_0 \approx \omega_{FT}/2\pi \approx 10^{13}/\text{s}$ . With these parameters we can reproduce the observed  $Y(F)$ . However, we note that a change in the prefactor  $R_0$  by one order of magnitude can be compensated by a small change in the activation barrier by a few millielectron volt with nearly the same good fit of the experimental data. Thus  $R_0$  is not accurately determined by our fit but the value we use is consistent with what is expected from theory.

Figure 3 compares the experimental (red circles) and the calculated  $Y(F)$  (black solid curve) using  $T_{FT}(t)$  obtained for (a) electronic heat transfer only (dashed green curve using  $\eta_{FT}=0.016/\text{ps}$ ,  $\eta_{FT,FR}=1.2/\text{ps}$ , and  $\eta_{ph,FT}=0$ ), (b) phononic heat transfer only (dashed blue curve  $\eta_{FT}=\eta_{FT,FR}=0$  and  $\eta_{ph,FT}=0.07/\text{ps}$ ), and (c) both heat transfers (black solid curve).

Although the process (b) seems to give better agreement with the experimental result than the process (a) at  $F=4.0-4.4$  J/m<sup>2</sup>, the deviation from the experimental results becomes noticeable with  $F$ . At  $F=4.4$  J/m<sup>2</sup> the process (a) or (b) alone reproduces the experimental result. Neither (a) nor (b) alone, however, does fit the experimental result for  $F=4.5-4.9$  J/m<sup>2</sup>, where the process (c) gives a nice agree-

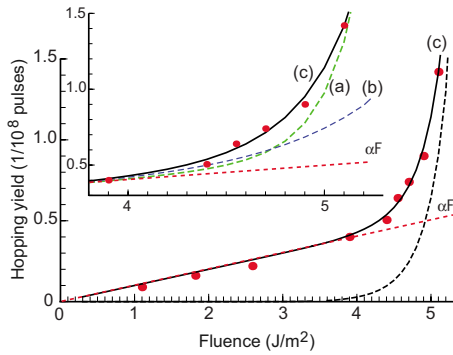


FIG. 3. (Color online) Calculated (black solid curve) and experimental result (red circles) of CO hopping yield as a function of fluence. Red (black) dashed line (curve) shows the first (second) term in  $F(Y)$  [Eq. (4)]. The inset is enlarged in  $F=3.8\text{--}5.2\text{ J/m}^2$  for different heat transfer processes [(a) effective electronic friction coupling (dashed green curve), (b) phonon coupling (dashed blue curve), and (c) both (black curve)]. See the text for the parameters used herein.

ment with the experimental result. The process (a) becomes dominant over the process (b) around  $F=4.7\text{ J/m}^2$  and the contribution of the process (b) is almost negligible above  $F=5.0\text{ J/m}^2$ . The calculated  $Y(F)$  confirms that heat transfers from both hot electrons and phonons cooperatively are responsible for CO hopping and explains the nonlinear increase in  $Y(F)$  above  $F\approx 4\text{ J/m}^2$ . From Fig. 3 we find that although hot electrons always play a role in the fluence range we studied, the phonon heat transfer plays indispensable role in order to achieve an agreement with the experimental result, except at the highest fluence where the phonon contribution becomes almost negligible. The change in the relative importance of the electronic and the phononic heating of the FT mode arises from a fact that  $\eta_{\text{eff,FT}}$  of the FT mode depends on  $F$  due to the intermode coupling of the FR mode.

Since the details of the heat transfer processes are washed away after integration  $R(t)$  over time, we study the transient behavior of  $R(t, F)$  for the processes (a)–(c) in order to gain an insight into the details of  $Y(F)$ . Figure 4 shows  $R(t, F)$  calculated for (a), (b), and (c) at  $F=4.3, 4.7, 5.0,$  and  $5.3\text{ J/m}^2$ . The different time scales of the electronic [ $\eta_{\text{eff,FT}}(t)=0.016\text{--}0.2/\text{ps}$  for  $F=4.3\text{ J/m}^2$ , and  $0.016\text{--}0.32/\text{ps}$  for  $F=5.3\text{ J/m}^2$ ] and the constant phononic ( $\eta_{\text{ph}}=0.07/\text{ps}$ ) heat transfer allow us to study which heat transfer plays a predominant role in driving hopping motion. At  $F=4.3\text{ J/m}^2$  the phonon coupling gives slightly larger hopping yield than the electronic coupling. Here we note that the hopping motion in the presence of phonon heat transfer has a shorter duration than that solely driven by the electronic one. This is because the cooling rate of the FT mode becomes faster in the presence of the phonon heat sink in the substrate. Although the electronic and phononic heat transfer give the almost same  $Y(F)$  at  $F=4.7\text{ J/m}^2$ , the corresponding  $R(t)$  exhibit quite different transient behaviors (it shows a long-lived hopping over 100 ps for electronic heat transfer while it shows a peak at 50 ps). As  $F$  becomes larger, the electronic heating becomes more important than the phononic heating. The growing rise of  $R(t)$  around 1 ps is due to a fact that  $\eta_{\text{eff,FT}}(t)$  increases with  $F$  through the in-

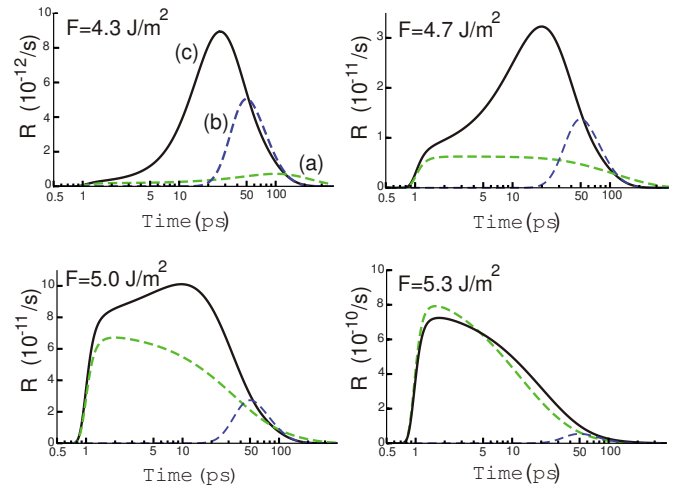


FIG. 4. (Color online) Transient behavior of hopping rate  $R(t)$  calculated for the heating process (a) electronic (dashed green curve), (b) phononic (dashed blue curve), and (c) both (black curve). See the text for the parameters used herein.

crease in the temperature of the FR mode. The time evolution of  $R(t, F)$  shows that phononic heating can be neglected for  $F\approx 5.3\text{ J/m}^2$ , where  $R(t)$  shows a rapid increase around 1 ps followed by the gradual long-lived decay. To our knowledge, such activated time evolution of a reaction driven by ultrafast laser excitation is quite unique for CO hopping on Cu at low  $F$  as studied in Ref. 3, in which the FT mode with very weak friction coupling is cooperatively heated by intermode coupling to the FR mode and by the substrate phonons.

For lateral hopping on a surface, we expect that the adsorbate needs sufficient excitation in a direction parallel to the surface for hopping and intuitively we might expect that only the translational mode is responsible. There is no doubt that the reaction pathway involves translational motion, which is populated thermally even at low temperatures and/or even at weak friction coupling to hot electrons. It is generally observed that for CO adsorbed on metals the electronic friction of the FT mode is much smaller than for the FR mode, and the other adsorbate vibrational modes. The potential-energy surface for CO adsorption on metals is usually very flat, in particular for adsorption on noble metals. This may indicate that a jellium type of picture may be valid as a first approximation. Within the jellium model, where the ions of the substrate are smeared out into a semi-infinite continuum, the energy of the adsorption bond does not change during CO parallel translation and the magnitude of the orbital matrix elements, which couple the CO to the substrate, are constant. However, the phase of the matrix element changes and in the jellium picture this is the origin of the nonadiabatic coupling which results in the damping of the FT mode. For the FR mode (and the other CO vibrational modes) the situation is very different since for these modes also the magnitude of the CO-metal coupling matrix elements changes with the vibrational normal-mode coordinate. We believe that the origin for why  $\eta_{\text{FR}}$  is stronger than  $\eta_{\text{FT}}$  is related to this qualitative difference in the nature of the mode coupling to the substrate electrons.

The mode-coupling parameter  $\eta_{\text{FT,FR}}$  we used in order to

fit the experimental data is larger than one what would expect from the simple qualitative arguments presented in Ref. 11. We believe that this may be due to strong coupling between the CO translational and rotational degree of freedom in the vicinity of the transition state, i.e., close to the top of the barrier along the reaction coordinate. Electronic structure calculations have shown that as the center of mass of the CO molecule is displaced from one symmetry site to another along the path in configuration space which minimizes the total energy, the C-O bond tilts away from the surface normal, initially slowly but close to the transition state very fast, as a function of the lateral CO position.<sup>18</sup> This may enhance the mode-coupling parameter  $\eta_{FT,FR}$  close to the transition state. In addition, the study by Dobbs and Doren<sup>12</sup> indicates that kinetic effects may be important close to the transition state. That is, because of the moment of inertia of the CO molecule, close to the transition state the CO molecular axis may be oriented differently than expected from the ground-state potential surface, which could also enhance the energy transfer between the translational reaction coordinate and the CO frustrated rotation.

Our model with intermode coupling between the FT and FR modes and phonon heat transfer to/from the FT mode can nicely reproduce the nonlinear increase in the CO hopping on Cu(111) at high fluence region. The temperature-

independent friction model with two anharmonically coupled modes is the one that captures the essential elementary processes behind hopping of CO molecules and atomic oxygens on the stepped PT surfaces<sup>11,19,20</sup> It is found that phonon heat transfer plays indispensable role in order to reproduce the experimental result except at high fluence. This model can also be applied for Cu(110), where the observed surface hopping observed at  $F=30$  J/m<sup>2</sup> has been found to be driven by the high electronic temperature.<sup>1</sup> Nonlinear spectroscopies such as two-pulse correlation using time-delayed two pulses<sup>9</sup> (this experiment permits us to estimate the time scale of reaction) and/or time-resolved real-time monitoring of  $R(t)$  (Ref. 2) are desired in order to elucidate a role played by electronic and phonon heating for CO hopping on Cu(111) at quite low laser fluences compared to similar experiments for CO on Pt(111).<sup>2,9</sup>

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